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(54) Method for producing novel phthalocyanine dye

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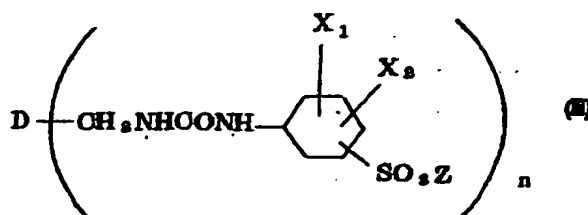
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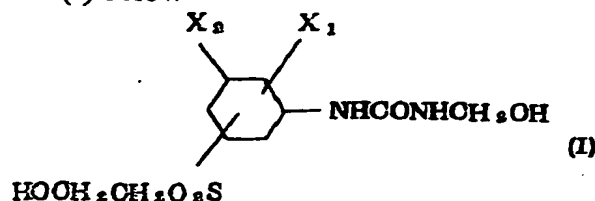
Detailed Description of the Invention

The present invention relates to a process for producing a novel phthalocyanine dye. More particularly, the present invention relates to a process for producing a novel phthalocyanine dye denoted by general formula (III) below



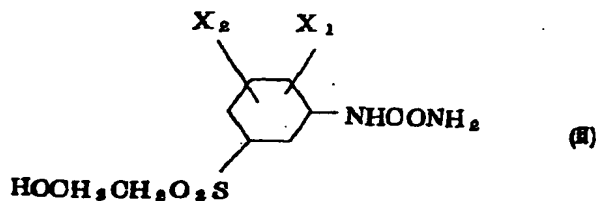
(here, each of X_1 and X_2 denotes hydrogen, or a lower alkyl, lower alkoxy, halogen, sulphonic acid, or carboxylic acid group, D denotes a phthalocyanine dye residue, Z denotes a $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ or $-\text{CH}=\text{CH}_2$ group, and n denotes a number of 1 or more)

by reacting a phthalocyanine dye having a replaceable hydrogen atom with a compound denoted by general formula (I) below



(here, X_1 and X_2 have the same meaning as above)

in sulphuric acid and treating with alkali if necessary, or reacting the above-mentioned dye and a compound denoted by general formula (II) below



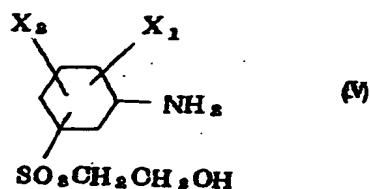
(here, X_1 and X_2 have the same meaning as above)

together with formaldehyde or a formaldehyde condensation product such as paraformaldehyde in sulphuric acid, and treating with alkali if necessary.

Dyes having an $-SO_2CH_2CH_2OSO_3H$ or $-SO_2CH=CH_2$ reactive group, so-called reactive dyes, are known as being suitable for the coloration of fibres from, for example JP-B-26-1089, JP-B-31-1643, and JP-B-31-9341, but the present inventors have investigated the relationship between the structure of this type of dye and the colouring characteristics, together with the method for introduction of the reactive group, and found that novel phthalocyanine dyes denoted by the above-mentioned general formula (III) are easy and inexpensive to produce by an industrially completely new method, and in addition have extremely good colouring characteristics and lightfastness properties.

The dyes obtained by the method of the present invention are suitable for the coloration of various natural or man-made fibres such as cotton, linen, viscose, and staple fibre, polyvinyl alcohol fibre etc., and give coloured products with excellent fastness to sunlight and humidity.

Compounds denoted by the above-mentioned general formula (I) or (II) that can be used in the present invention are prepared as follows. That is, using a method described in for example Organic Synthesis Vol 31 p 8 (1951), treating a known amine denoted by general formula (IV) below



(X_1 and X_2 have the same meaning as above)

using sodium cyanate or urea gives a compound denoted by the above-mentioned general formula (II), and by further carrying out a methylation process at normal pressure using, for example, formaldehyde in a weakly alkaline aqueous solution at 30°C to 40°C, gives a compound denoted by the above-mentioned general formula (I), and both can be obtained in good yield. As compounds denoted by the above-mentioned general formula (I) or (II) obtained in this way, there can be cited as examples the following in which a urea group or a methylol urea group is at the 1-position on the phenyl group, and the type and position of $-\text{SO}_2\text{CH}_2\text{CH}_2\text{OH}$, X_1 , and X_2 are shown.

$-\text{SO}_2\text{CH}_2\text{CH}_2\text{OH}$	X_1	X_2
3	H	H
4	H	H
3	6-OCH ₃	H
"	6-CH ₃	H
"	6-COOH	H
"	6-SO ₃ H	H
"	6-Cl	H
"	4-OCH ₃	H
"	4-OCH ₃	6 OCH ₃
4	6-COOH	H
"	3-CH ₃	H
"	3-CH ₃	6 CH ₃
"	3-CH ₃	6 OCH ₃
"	3-OCH ₃	6-OCH ₃
"	3-OC ₂ H ₅	6-OC ₂ H ₅

As the phthalocyanine dye residue used in the present invention there are dyes such as metal phthalocyanines containing copper, nickel, cobalt, etc., and in some cases metal-free phthalocyanine dyes, having a replaceable active hydrogen on a phthalocyanine phenyl nucleus or on a sulphonamide, carbonamide, aminotriazinyl, urea, etc. group. Here, as the phthalocyanine dye having a replaceable active hydrogen atom on a phenyl nucleus there are, for example, the following.

Phthalocyanine -(3)-sulpho-(3)-trisulpho-N-phenylamide

Phthalocyanine-(3)-sulpho-(3)-sulphonamide-(3)-disulpho-N-phenylamide

Phthalocyanine-(3)-sulpho-(3)-disulpho-N-benzylamide

(3)-Di(*p*-methylphenylaminomethyl)phthalocyanine-(3)-disulphonic acid

(4)-Tetraphenoxy phthalocyanine

(4)-Tetraphenyl phthalocyanine

Furthermore, as phthalocyanine dyes having a replaceable active hydrogen atom on a sulphonamide, carbonamide, aminotriazinyl, urea, etc. group there are, for example, the following.

Phthalocyanine-(3)-sulpho-(3)-trisulphonamide

Phthalocyanine(3)-sulpho-(3)-disulphonamide-(3)-sulpho-N-(β -hydroxyethyl)amide

Phthalocyanine(3)-disulpho-(3)-disulpho-N-(*p*-sulphamylphenyl)amide

Phthalocyanine(3)-disulpho-(3)-disulpho-N-(*m*-sulphamylphenyl)amide

Phthalocyanine(3)-disulpho-(3)-disulpho-N-(*p*-carbamylphenyl)amide

Phthalocyanine(3)-disulpho-(3)-disulpho-N-carbamylamide, etc.

These representative examples are explained in Examples.

By reacting these phthalocyanine dyes and the above-mentioned general formula (I) or the above-mentioned general formula (II) with formaldehyde or a condensation product such as paraformaldehyde in sulphuric acid, novel phthalocyanine dyes denoted by the above-mentioned general formula (III) in which the active hydrogen in the phthalocyanine dye is replaced are obtained. The reaction is carried out in 80% or greater concentration sulphuric acid or low concentration fuming sulphuric acid at a temperature of 40°C or below for a few hours or a few tens of hours.

In order to obtain $-\text{CH}=\text{CH}_2$ as the group Z in the above-mentioned general formula (III), the product where Z is $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$, which is obtained by carrying out a condensation reaction in sulphuric acid, is subjected to a weakly alkaline treatment.

In the reaction using the above-mentioned general formula (II) in sulphuric acid, amide methylation can be carried out by a methylolating reagent that is added at the same time, and the same kind of product as that obtained when using the above-mentioned general formula (I) is obtained.

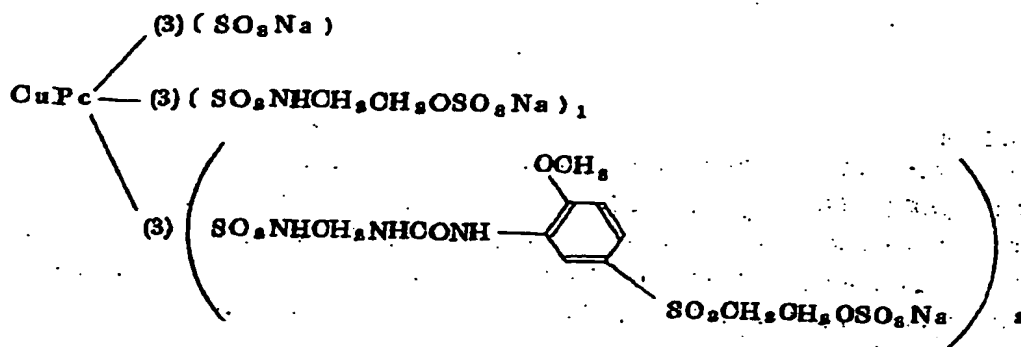
In order to increase the solubility of the novel phthalocyanine dye thus obtained denoted by the above-mentioned general formula (III), further sulphonation may be carried

out if required by dripping fuming sulphuric acid into the sulphuric acid reaction solution, or by low concentration fuming sulphuric acid after first taking out the dye.

The present invention is explained specifically below by means of Examples.

Example 1

9.4 parts of copper phthalocyanine-(3)-sulpho-(3)-disulphonamide-(3)-sulpho-N-(β-hydroxyethyl)amide was dissolved in 94 parts of 100% sulphuric acid, to this was added 5.5 parts of N-[3-(β-hydroxyethylsulphonyl)-6-methoxyphenyl]-N'-methylol urea, after stirring for 3 hours at 20°C the reaction solution was discharged into 600 parts of ice water containing 60 parts of potassium chloride, after filtering off the precipitate the damp cake was suspended in 150 parts of a 10% aqueous solution of potassium chloride, and after neutralising the solution to pH 6 to 7 with soda ash and filtering a dye denoted by the structural formula below and having a reddish turquoise blue hue was obtained.

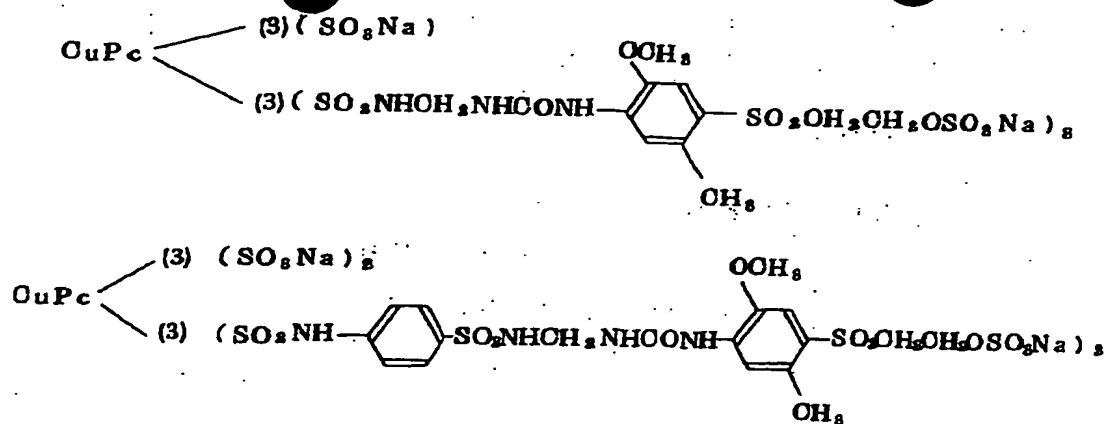


(CuPc denotes copper phthalocyanine)

Example 2

8.9 parts of copper phthalocyanine-(3)-sulpho-(3)-trisulphonamide was dissolved in 89 parts of 100% sulphuric acid, to this were added 7.5 parts of N-[4-(β-hydroxyethylsulphonyl)-6-methoxy-3-methylphenyl]urea and 3.0 parts of a 30% aqueous solution of formalin, after stirring for 10 hours at 15°C to 20°C, the reaction solution was discharged into 500 parts of ice water containing 50 parts of sodium chloride, after filtering off the precipitate the damp cake was suspended in 150 parts of 15% brine, and after neutralising the solution to pH 6 to 7 with soda ash and filtering a dye denoted by the structural formula below and having a reddish turquoise blue hue was obtained.

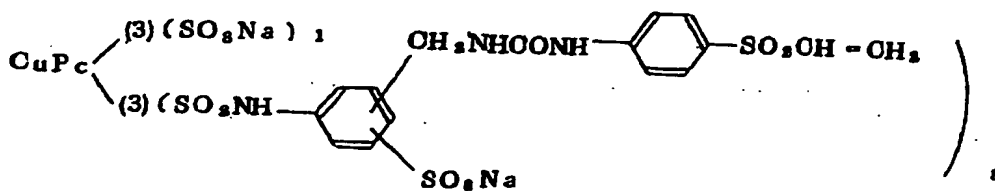
If instead of the 8.9 parts of copper phthalocyanine-(3)-sulpho-(3)-trisulphonamide used here, 12.1 parts of copper phthalocyanine(3)-disulpho(3)-disulpho-N-(p-sulphamylphenyl)amide was used, a dye having a turquoise blue hue was obtained.



Example 3

11.2 parts of copper phthalocyanine-(3)-sulpho-(3)-trisulpho-N-phenylamide was dissolved in 67 parts of 90% sulphuric acid, to this were added 4.3 parts of N-[4-(β -hydroxyethylsulphonyl)phenyl]urea and 0.6 parts of paraformaldehyde, and after reacting at 20°C to 25°C for 5 hours, sulphonation was carried out by adding dropwise 50 parts of 65% fuming sulphuric acid while cooling to 10°C or below and then stirring for 1 hour at 10°C.

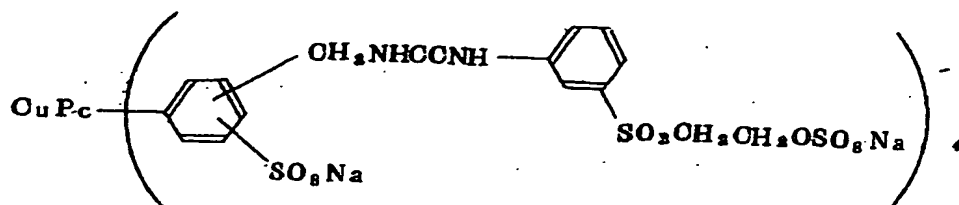
The reaction solution was discharged into 700 parts of ice water containing 70 parts of sodium chloride, after filtering off the precipitate the damp cake was suspended in 150 parts of a 20% aqueous solution of sodium chloride, and after neutralising the solution to pH 9 with soda ash, then stirring for 1 hr while maintaining the pH at 9 by adding soda ash and filtering, a dye denoted by the structural formula below and having a turquoise blue hue was obtained.



Example 4

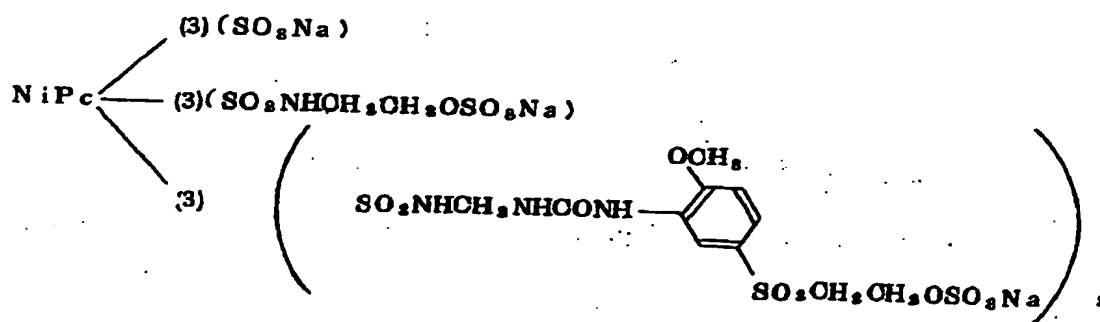
8.8 parts of tetraphenyl copper phthalocyanine was dissolved in 53 parts of 90% sulphuric acid, to this were added 4.3 parts of N-[3-(β -hydroxyethylsulphonyl)phenyl]urea and 0.6 parts of paraformaldehyde, and after reacting at 15°C to 20°C for 10 hours, sulphonation was carried out by adding 4.0 parts of 65% fuming sulphuric acid dropwise with cooling to 10°C or below and then stirring for 1 hour at 10°C. The reaction solution was discharged into 600 parts of ice water containing 60 parts of sodium chloride, after filtering off the precipitate the damp cake was suspended in 150 parts of 15% brine, and after

neutralising the solution to pH 6 to 7 with soda ash and filtering a dye denoted by the structural formula below and having a green hue was obtained.



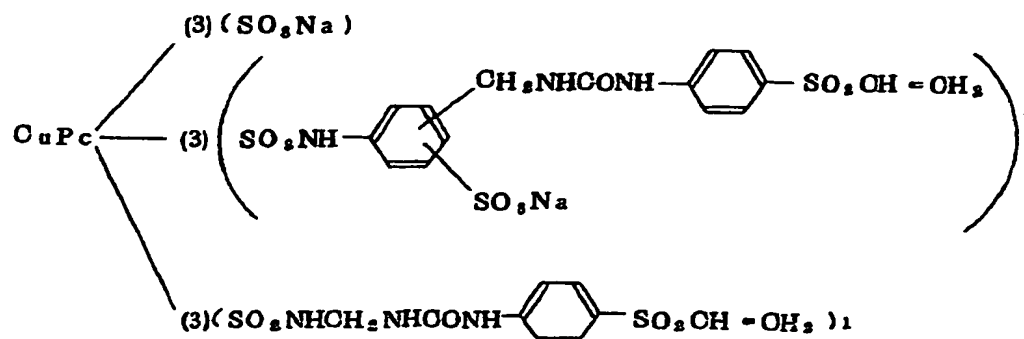
Example 5

The process of Example 1 was carried out in exactly the same way except that 9.4 parts of nickel phthalocyanine-(3)-sulpho-3-sulphonamide-3-sulpho-N-(β-hydroxyethyl)amide was used instead of the 9.4 parts of copper phthalocyanine-(3)-sulpho-(3)-disulphonamide-(3)-sulpho-N-(β-hydroxyethyl)amide, and a dye denoted by the structural formula below and having a bluish green hue was obtained.



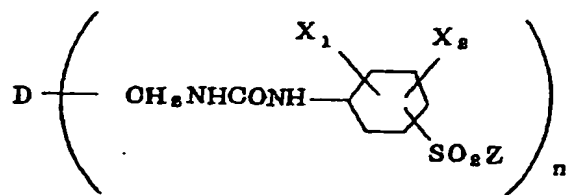
Example 6

The process of Example 3 was carried out in exactly the same way except that 10.4 parts of copper phthalocyanine-(3)-sulpho-(3)-sulphonamide-(3)-disulpho-N-phenylamide was used instead of the 11.2 parts of copper phthalocyanine-(3)-sulpho-(3)-trisulpho-N-phenylamide, and a dye denoted by the structural formula below and having a turquoise blue hue was obtained.

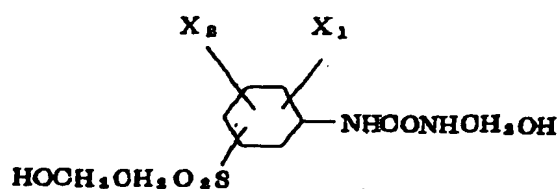


Claim

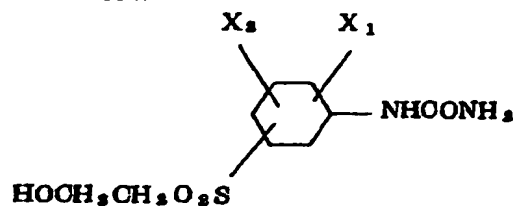
1 A process for producing a novel phthalocyanine dye denoted by the general formula below



(here, each of X_1 and X_2 denotes hydrogen, or a lower alkyl, lower alkoxy, halogen, sulphonic acid, or carboxylic acid group, D denotes a phthalocyanine dye residue, Z denotes a $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ or $-\text{CH}=\text{CH}_2$ group, and n denotes a number of 1 or more) by reacting a phthalocyanine dye having a replaceable hydrogen atom with a compound denoted by the general formula below



(here, X_1 and X_2 have the same meaning as above) in sulphuric acid and optionally further treating with alkali, or reacting the above-mentioned phthalocyanine dye and a compound denoted by the general formula below



(here, X_1 and X_2 have the same meaning as above) together with formaldehyde or a formaldehyde condensation product such as paraformaldehyde in sulphuric acid and optionally further treating with alkali.